A Miniature Quadrupole Mass Spectrometer Array and GC For Space Flight: Astronaut EVA and Cabin-Air Monitoring

A. Chutjian, M.R. Darrach, V.Garkanian, S.P. Jackson, T.D. Molsberry, O.J Orient and D. Karmon
Jet Propulsion Laboratory, California Institute of Technology

P.M. Holland
Thorleaf Research, Inc.

D. Aalami
Space Instruments Inc.

ABSTRACT

A miniature quadrupole mass spectrometer array and gas chromatograph have been designed and built for NASA flight missions. Without the gas chromatograph the mass spectrometer is to be used for detection, by astronauts in EVA, of N_2, O_2, the hydrazines, and NH_3 leaks in the hull of the International Space Station, and of adsorbed hydrazines on the astronauts' suits. The fully-adapted astronaut system, with all software and visual readout, is called the Trace Gas Analyzer. When interfaced with the miniature gas chromatographic system, the mass spectrometer will be useful for a variety of NASA missions involving more complex gas mixtures. The missions include planetary exploration (to Venus, Europa, Titan, *etc.*), as well as cabin-air monitoring for long-duration human flight to the Moon, Mars, and beyond. A description of the miniature mass spectrometer, the Trace Gas Analyzer system and miniature gas chromatograph front end is given, and test results are shown for a variety of gas mixtures. A variety of possible flight applications is discussed.

INTRODUCTION

Miniature mass spectrometry is a powerful tool for identifying atomic, molecular, and biological species, and their abundance, in a plasma, complex atmosphere, liquid, subsurface, or on a surface. With suitable front ends [*e.g.*, a gas chromatograph for gas mixtures, or a microextraction system for volatile organic compounds (VOCs) dissolved in liquids] the mass spectrometer (MS) will find use in long-duration human flight (LDHF) to monitor in the spacecraft the atmosphere, the quality of drinking water, and the microbial content of the air and surfaces. In robotic planetary missions one can study atmospheres and geology of outer planets and satellites, where missions are sensitive to the mass, power, and volume of instruments [1,2]. Within *NASAs Advanced Environmental Monitoring and Control Program* (AEMC) detection of trace toxic species in the air and water supply are crucial to astronaut survival in LDHF. As a result, there are presently aboard the International Space Station (ISS) more than six different types of sensors for vapor detection. These are: (1) a magnetic sector as the Major Constituents Analyzer (MCA), (2) a quadrupole MS for medical monitoring (breath analysis), (3) a proposed ion-mobility spectrometer (IMS) with two gas chromatographs (GCs) for monitoring cabin air, (4) a variety of CO detectors and smoke alarms[3], (5) a GC/IMS for use in the ISS and shuttle airlocks for hydrazine detection, and (6) Draeger tubes (currently the only approved means of hydrazine detection in airlocks). Some of these units (the MCA, quadrupole, and ion-mobility spectrometer) occupy about 1-2 racks each on the ISS. *There would be a significant savings in mass, volume, power and cost -- with no loss in performance -- if these sensors could be replaced by a single, miniature mass spectrometer array*. Future expansions of the ISS, or for that matter of any space capsule, will be more reasonably and economically met by instrument shrinkage, rather than by physical expansion of the capsule itself. Moreover, miniature MSs could be placed in each module or compartment for fast response and high localization. On missions to Mars and beyond, where commodities will be at a premium, such savings are crucial to mission viability and success.

The present generation of quadrupole MSs being flown on *Galileo* and *Cassini* are based on 1970s technology. They weigh approximately 9-12 kg and consume about 25 watts power. With smaller MSs (mass about 1 kg and power of 3-6 watts) one can plan higher-velocity missions to the outer planets and moons, especially to Jupiter, Europa, Saturn, Titan, Pluto, and Triton where one expects a dynamic and complex

mixture of gases. One can even consider *multiple* MSs, for example into Io's orbit to measure the time evolution of the torus plasma, especially after a volcanic eruption on Io.   Another benefit of miniature spectrometers is realized in a *landed* package where the small size of the device, and its survivability to large *g*-forces, enables science measurements that cannot be contemplated now. Mars, asteroid, and comet surface penetrators can benefit from a miniaturized, survivable oven/GC/calorimeter interfaced to an MS.   Use of a miniature GC can confirm species

The requirements for ISS cabin air and water purity are given by Ganapathi *et al.* (1996). Requirements are in terms of *Spacecraft Maximum Allowable Concentrations* (SMACs) for air, and *Spacecraft Maximum Contaminant Levels* (SMCLs) for water. The species on the SMACs list includes majority species (H_2, CO, CH_4, O2, H_2O, CO_2 and N_2) present at the 10-7000 ppm levels. There are also approximately 40 trace species on the SMACs list, and are in the concentration range 0.02 ppm (acrolein) to 1000 ppm (ethanol), and include, for example, acetaldehyde (2 ppm), methanol (7 ppm), acetone (22 ppm), xylenes (50 ppm), dichloromethane (3 ppm), and vinyl chloride (1 ppm).   Any MS must also be capable of detecting the hydrazines, as these are toxic species which can be brought into the cabin *via* adsorption of engine fuels on the astronaut's extravehicular mobility unit (spacesuit, EMU) after a space walk.   The SMCL (water) species include benzene (limit at the 5 µg/L level), 1,2-dichlorobenzene (600 µg/L), CCl_4 (5 µg/L), and toluene (2000 µg/L). It is evident that, given the complex mixture of species involved and their broad concentration range, a GC system must be developed which will have a capability for preconcentration, and be usable in good part for both air- and water-quality monitoring. It must have a selectivity to electron-attaching species (the freons, chloroform, CCl_4) for use with an MS operating in its *negative-ion* as well as *positive-ion* mode. Finally, the GC must be consistent with the mass, volume, and power of the present generation of miniature MSs. The miniature quadrupole mass spectrometer array (QMSA) system[4], with the appropriate GCs, is capable of separating the approximately 40 major and minor trace-air species, and approximately 20 trace-water species.

MAIN SECTION

The QMSA[1,2] consists of a miniature electron-impact ionizer, quadrupole mass-filter system, and a miniature channel-type electron multiplier and is shown schematically in Fig. 1.   The mass-filter itself consists of 16 rods, each 2mm dia and 25 mm long. They are arranged in a 4 X 4 pattern to form nine quadrupolar regions.   The miniature electron-impact ionizer is designed for high efficiency, where ions are extracted and focused only into the nine quadrupole entrance apertures and where all elements of the ion lens stack contain nine lenslets.   The electron and ion trajectories for the parallel lenslets were computed using a full three-dimensional, space-charge limited field-and-trajectories

code[5] . The properties of the QMSA are 1500g mass, 15 watts power, and of dimensions 30 cm (P) H 12 cm (*w*) H 8 cm (*h*). These power and dimensions correspond to the use of commercial off-the-shelf electrical components and further miniaturization efforts are planned to reduce the size and power by a factor of 3. When operated in single ion monitoring the QMSA has a sensitivity of 2 x 10^{12} counts/torr/sec and is currently undergoing a redesign to yield a 10x improvement in efficiency.   When used in EVA the QMSA is integrated into the Trace Gas Analyzer (TGA) which currently enables an astronaut to detect leaks of ammonia, the hydrazines, N_2, and O_2. A picture of the QMSA sensor package is shown in Fig. 2. The TGA is scheduled to fly on ISS Mission 5A, supporting the first flight where ammonia will present to charge a cooling system.   A total of four units are to be delivered, two of which will be maintained in orbit, ready to be used in the event of a leak.
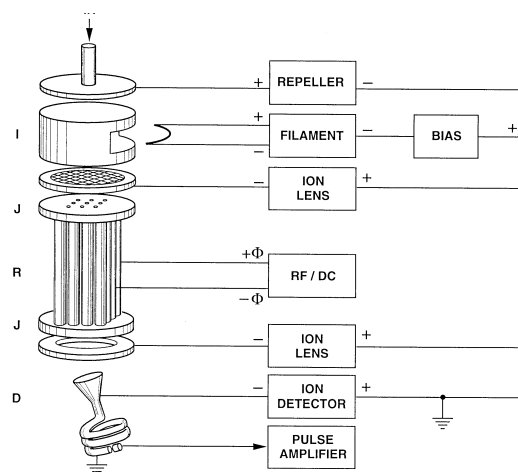

Figure 1.   Schematic diagram of miniature QMSA. Additional legend is: **I**, ionizer; **J**,   quadrupole rod alignment jig; **R**, quadrupole rod array; **D**, channel electron multiplier.

An overview diagram of the initial test configuration of the full GC/QMSA system is shown in Fig. 3.   The system was designed to include a GC/QMSA interface, approaches for controlling flow rates into the QMSA, separations using various types of interchangeable GC capillary columns, use of MEMS (micro-electromechanical systems)-based GC injections, a miniature sampling pump and inlet, and simple computer/electronic control of the MEMS-based GC system. This illustrates   the sample inlet, MEMS injector, sampling pump, GC column and the QMSA with its vacuum pump. A design modification can include a thermal-conductivity detector (TCD) placed between the column exit and the QMSA input, and a second QMSA input which bypasses the GC column completely (see below).
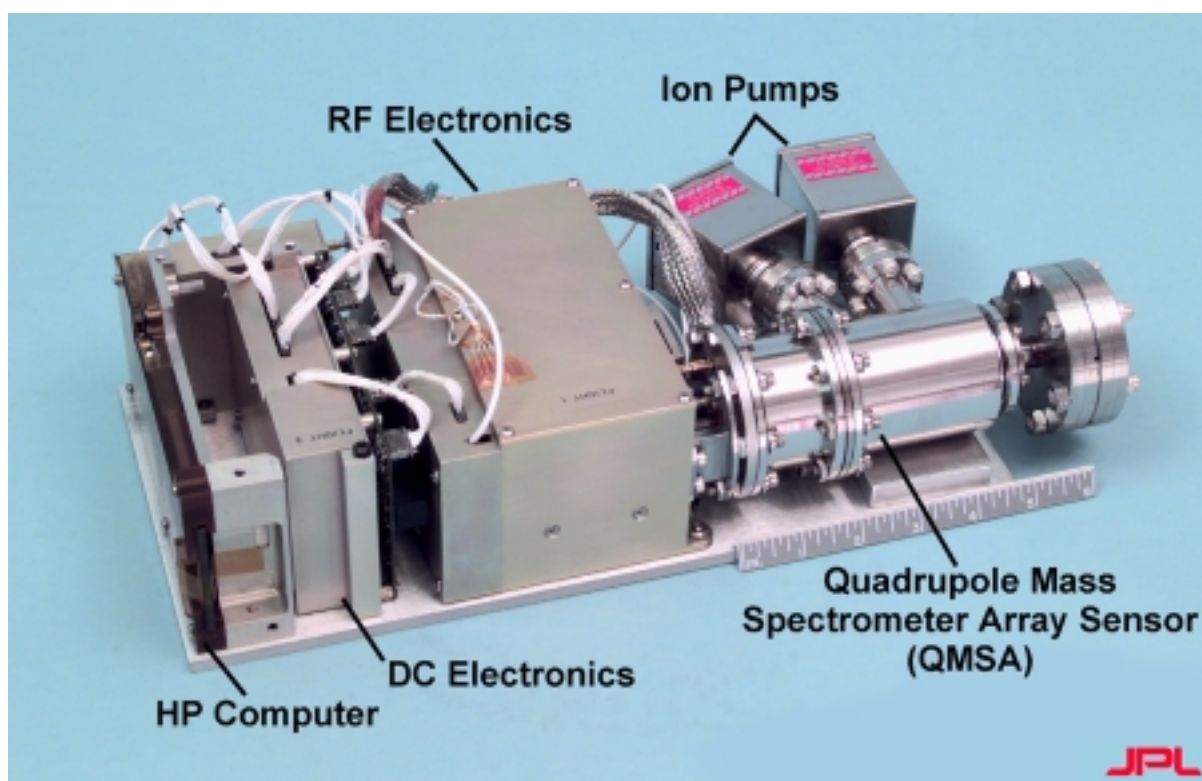
Figure 2. Photograph of the QMSA flight sensor. Note the vacuum flanges on the extreme right of the sensor are for vacuum integrity during shipping only.
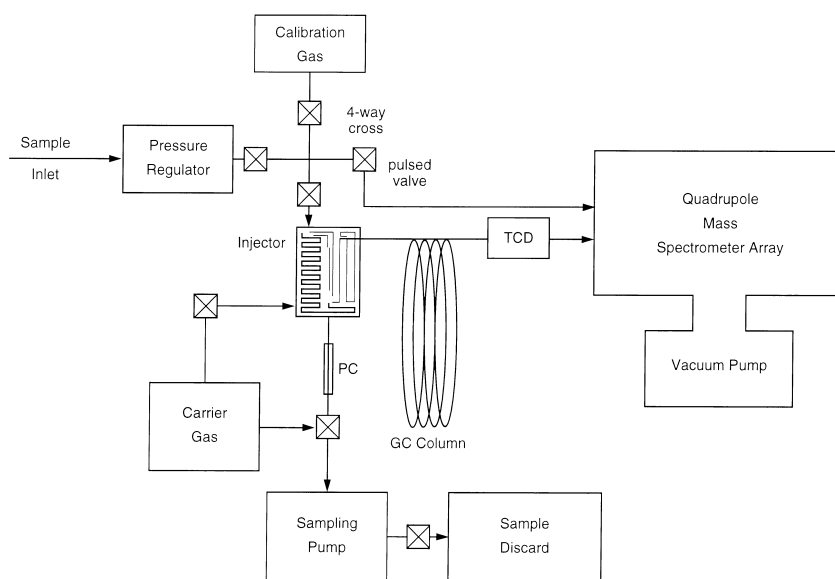

Figure 3. Overview diagram of miniature GC/QMSA system. Additional legend is: **GC**, gas chromatographic column; **TCD**, thermal conductivity detector; **PC**, miniature preconcentrator

A photograph of one GC/QMSA test configuration is shown in Fig. 4. From left to right this figure shows: gas sampling bag, miniature pressure regulator, miniature control valves and sampling pump, control electronics (below), MEMS injector, GC column assembly, GC/QMSA interface, and QMSA (with vacuum pump below table).

RESULTS

The GC/QMSA instrumentation was demonstrated in preliminary measurements using various test gas mixtures. Emphasis was placed in the first series of tests on mixtures simulating the Venus atmosphere. It consists of 96.5% CO_2 and 3.5% N_2, with trace components of SO_2, H_2O, Ar, CO, He, OCS, H_2S, HDO, HCP, *etc.*[6] Of the important Venus atmosphere components, perhaps the most difficult to separate by gas chromatography are molecular nitrogen (N_2) and carbon monoxide (CO) due to their similar chemical properties and retention times in many GC columns. The fact that these compounds have the same molecular weight with the dominant (parent ion) mass of both appearing at mass 28 (within 1:2300 mass units makes this especially challenging for QMSA detection. GC/QMSA results for this separation using a specialized Carboxen porous layer open tubular (PLOT) column are shown in Figure 3. Here, a "Venus mixture" of 200 ppm CO in CO_2 (97%) and N_2 (3%) was used, and the separation effected with the combined GC/QMSA with the column running at 25 C. The first peak eluted at times t #3m after opening of the sample injection valve corresponds to the ion N_2^+/ N_2. At t–3.5m the CO^+/CO species appears, followed by a large pressure rise in the QMSA caused by appearance of the majority CO_2 species, causing a large CO_2^+/CO_2 peak. This pressure rise can easily be eliminated with higher pumping speed within the QMSA enclosure. Elution time and peak widths can be reduced by running the column at elevated temperatures. The miniature GC has heaters and electronics already integrated enabling constant temperature or ramped temperature scanning.

Another important component of the Venus atmosphere, within a mixture that further tests the sensitivity of the present GC/QMSA system, is carbonyl sulfide (COS) in a primarily CO_2 atmosphere with some admixed N_2. Results of this GC/QMSA sample test are shown in Fig. 6. The QMSA was set to record the mass peak of 60 u corresponding to COS^+/COS. Neon and argon separations were also investigated at concentrations similar to those in the Venusian atmosphere. Results of this GC/QMSA sample test are shown in Fig. 7.

In terms of system dimensions and power, depending on the sophistication of design, the mass of the GC system alone is about 250-300 g. The required power including a thermal-conductivity detector, valves, sampling pump, column heater is about 200 mW and the dimensions are about 5 cm dia H 12 cm long. Compared to conventional GC coupled to mass spectrometers the miniature GC represents a reduction in mass, size, and power by factors of at least 10. Overall sensitivity of the GC/QMSA sensor is currently about 200 counts/ppm/sec when operated in single ion monitoring. The improved ionizer for the QMSA will increase the sensitivity to at least 2000 counts/ppm/sec. For cabin-air monitoring of SMAC species at the sub-ppb level the GC/QMSA will include a small preconcentrator (negligible size or power impacts) which has demonstrated to increase the sensitivity by a factor of 500. A critical concern for GC usage in space is the amount of carrier gas consumed which for a conventional GC is 30-50 ml/min at 15 psi, whereas the miniature GC consumes only 100 µl/min of carrier gas.

Finally, we note that other gas mixtures can be addressed, including mixtures of various SMACs species for LDHF cabin-air monitoring. Other flow paths can be tested. Referring to Fig. 3, one can include a TCD after the GC column exit, and a second input to the QMSA bypassing the GC completely. One may then have three viable paths to a measurement: (a) a complete GC-TCD-MS measurements, (b) in the event of a failure of the QMSA a GC-TCD measurement, and (c) in the event of a failure of the GC-TCD line an MS measurement alone. This flexibility is especially useful in hostile atmospheres (radiation at Jupiter, Io, Saturn and Titan; sulfuric acid and high temperatures at Venus) or in human-critical environments (a lunar outpost, or a Mission to Mars).

CONCLUSIONS

A miniature GC system in conjunction with a miniature quadrupole mass spectrometer array (QMSA) has been designed and tested. The system has shown excellent separation properties for N_2-CO-CO_2 mixtures using a Carboxen PLOT column; and a COS-N_2-CO_2 mixture using a divinylbenzene (*GSQ*) column. The initial design is flexible enough that other gas mixtures and system flow paths can be addressed.

ACKNOWLEDGMENT
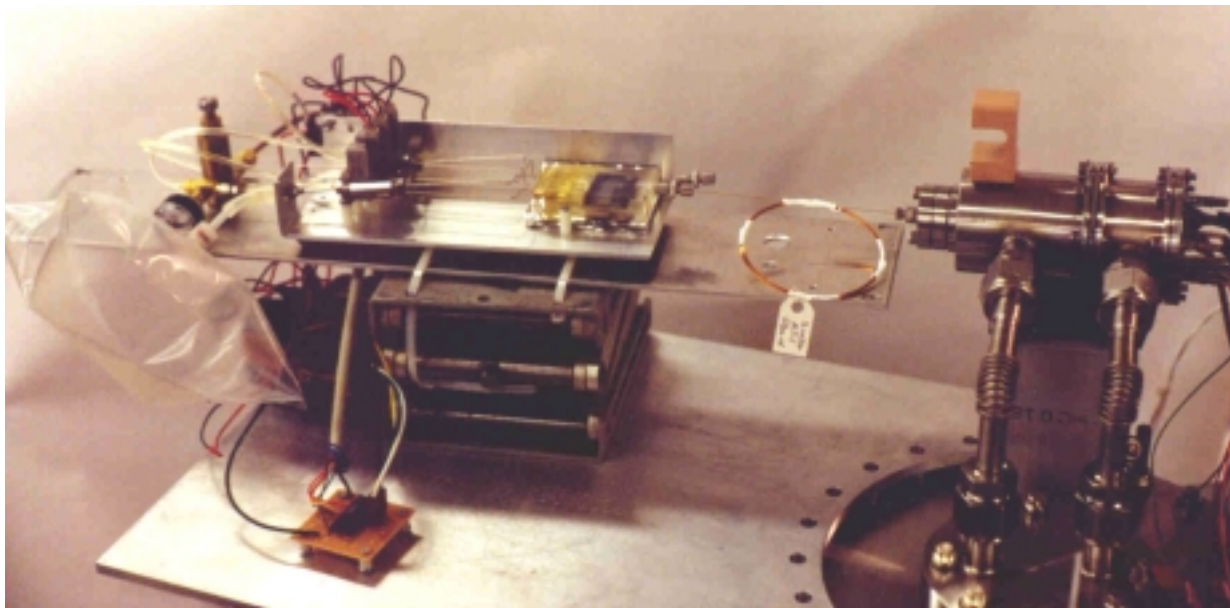
Figure 4. Photograph of the miniature GC/QMSA breadboard test configuration.

Carboxen Column GC-MS Discrimination Between CO and N_2
200ppm CO in 97% CO_2 + 3% N_2

N_2^+/N_2

x 10
CO^+/CO

CO_2^+/CO_2

Counts (Arb. Units)
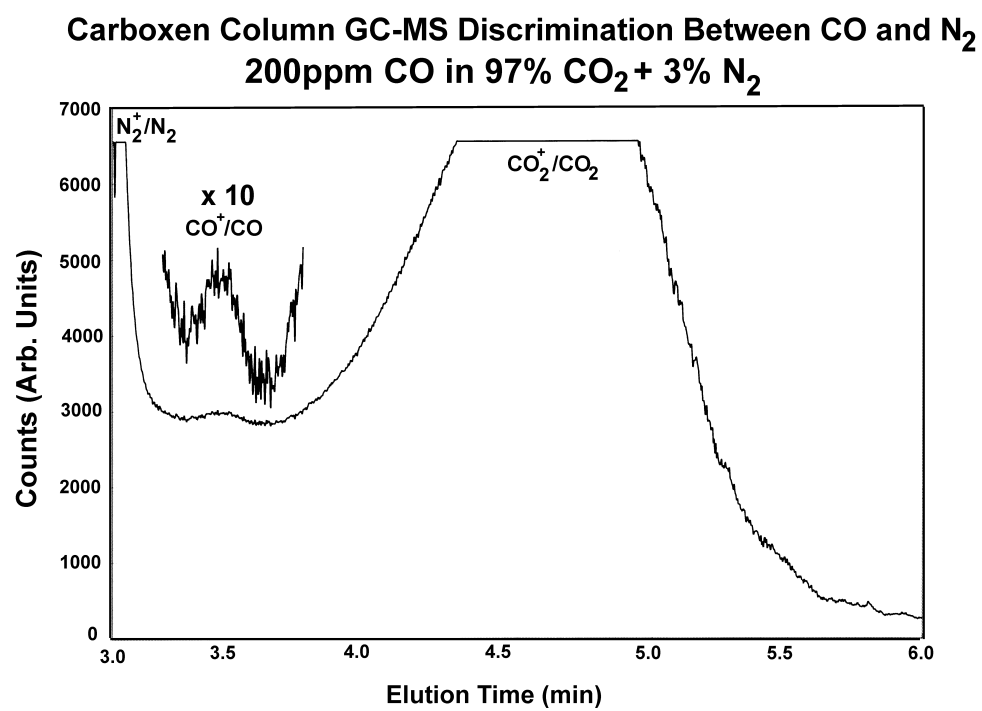
Elution Time (min)

Figure 5. GC/QMSA results for a Venus test mixture containing CO in CO_2 and N_2

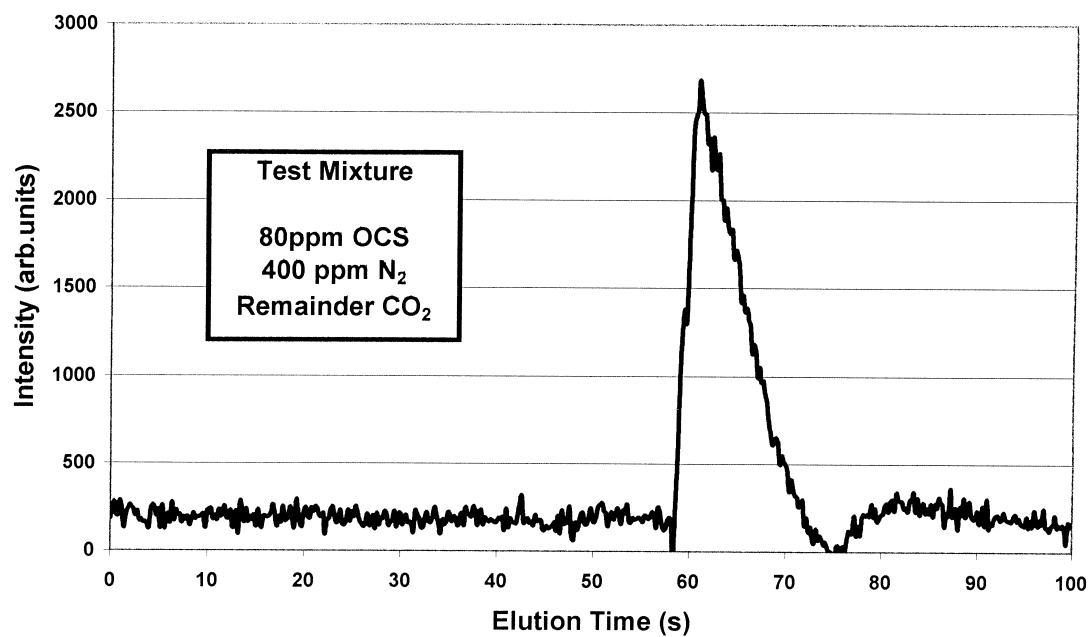**Figure 6**. **GC/QMSA spectrum of OCS in CO2 and N2.** The column stationary phase material is a porous divinylbenzene homopolymer.
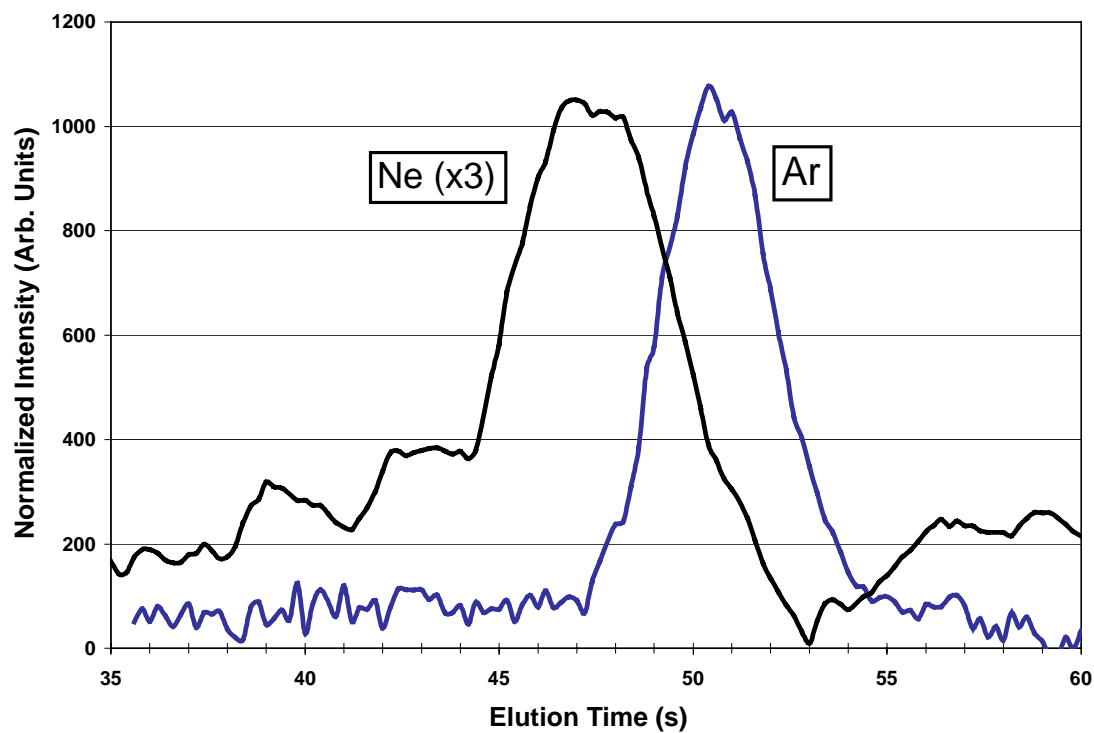

Figure 7. GC/QMSA spectrum of 50 ppm Ne and Ar (each) in CO_2.

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4. "Array" here means not just one quadrupole MS, but a $k\times k$ pattern of miniature MSs, where k can be as large as the manufacturing method allows. Arrays can be used to increase detection sensitivity and dynamic range: if one reduces linear dimensions by a factor k^{-1} (< 1), then the MS input aperture area, hence sensitivity, varies as k^{-2}. This loss is regained, and can be exceeded, by the k^2 array of parallel detectors.

5. J. Rouse, X. Zhu, and E. Munro, *SPIE Proc. 2522* (1995) p. 375.

6. K. Lodders and B. Fegley, *The Planetary Scientists Companion* (Oxford, London, 1998).